

COAL LIQUEFACTION WITH TIN OXIDE CATALYST

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INTRODUCTION

In recent years, a large amount of work has been performed in the region of coal chemistry. Liquefaction of coal has been investigated widely not only of industrial application but also fundamental interests. Various catalysts are examined in a huge amount of papers reported. They are classified into many categories. One of them is metal oxide catalyst. Metal oxide catalysts are easily prepared and handled. Iron oxide catalyst and HDS catalyst have been tested in pilot scale experiments. In this paper, we examined the catalytic activity of metal oxide catalysts for direct liquefaction of coal.

It is useful to investigate the mechanism of the liquefaction of coal using model compounds which are typical of coal. In the latter part of this paper, we examine the hydrogenation of benzyl ether and discuss the reaction path of liquefaction.

EXPERIMENTAL SECTION

Figure 1 shows the experimental apparatus used in this work. The autoclave was made of stainless steel. Coal or model compounds were mixed with solvent and catalyst in the autoclave by continuous stirring. The autoclave was heated up to reaction temperature at a rate of 50°C/min under pressurized hydrogen.

Liquid products were separated into three fractions by solvent extraction. That is, n-hexane soluble fraction was called oil, n-hexane insoluble and toluene soluble fraction was called asphaltene, and toluene insoluble fraction was called residue. Conversion of coal was calculated from the weight of residue (daf). Gas chromatography was used for analysis of gas and liquid products. Residue was analyzed by X-ray diffraction.

The composition of coals used in this work is shown in Table 1. Powdered coal (0.1 - 0.4 mm) was mixed with twofold of creosote oil. Catalysts were prepared by the following methods. That is, calcination of hydroxide (Fe_2O_3 , TiO_2 , MnO , ZnO , SnO_2) and impregnation method ($\text{Co-Mo-Al}_2\text{O}_3$, Ni-Mo-TiO_2). Powdered catalyst passed through a 200 mesh sieve was mixed with slurry in a ratio of 5 wt% to coal. Benzyl ether, phenyl ether, and dibenzyl were used as model compounds. They were added to 1-methylnaphthalene (MN) or tetralin and hydrogenated in the presence or absence of SnO_2 catalyst.

RESULTS AND DISCUSSION

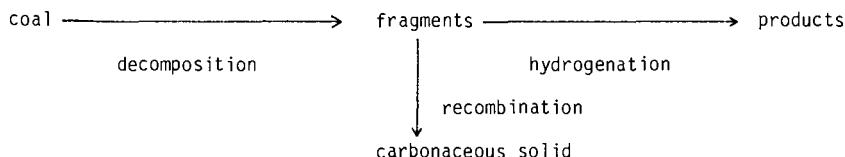
Coals were liquefied at 450°C for 30 min under pressure of 150 atm. Pressurized hydrogen was allowed to flow at a rate of 300 l/hr (stp).

Figure 2 shows the conversion of Taiheiyo coal liquefied with various catalysts. It was found that SnO_2 catalyst showed the highest activity, and that the conversion of coal and yield of oil reached 100% and 75%, respectively. Consequently the reactions with SnO_2 catalyst were examined in detail hereafter.

At first, three kinds of coal were liquefied with SnO_2 catalyst under the same conditions mentioned above. Conversion of coal is shown in Figure 3. It was found that the conversion of coal increases with the content of volatile matter.

It was found that catalyst distributed in residue was reduced to metallic tin from X-ray diffraction analysis. Therefore it was considered that catalyst present in coal mixture under reaction conditions is melted tin metal.

The following scheme is well-known as the reaction path for coal liquefaction.



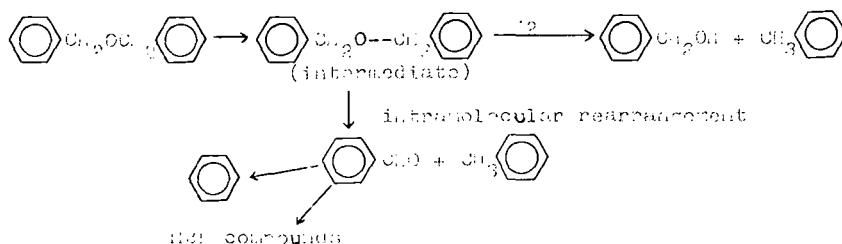
Scheme I

Coal is thermally decomposed to fragments followed by hydrogenation and recombination reactions. Fragments were recombined with each other to form carbonaceous solid which is one of the components of residue. When SnO_2 was used as catalyst, residue was not formed. It is considered that SnO_2 has higher selectivity for hydrogenation than for recombination. In order to confirm the reason we examined the hydrogenation of model compounds.

Benzyl ether was hydrogenated with or without SnO_2 catalyst under initial pressure of 150 atm. Figure 4 shows the gas chromatograms of products hydrogenated at 350°C in 1-methylnaphthalene. There are some differences in product distribution. In the presence of SnO_2 catalyst, benzyl ether decomposed to toluene and benzyl alcohol. Compounds which have higher boiling points than benzyl ether (called HBP compounds) such as fluoranthene were formed at low selectivity. On the contrary, the selectivity to HBP compounds increased in the absence of SnO_2 catalyst. Products from hydrogenation of benzyl ether with several catalysts are shown in Table 2. The selectivity to HBP compounds was found to be about 40% without SnO_2 catalyst, while in the presence of SnO_2 about 10%. It was also found that the selectivity was independent of the hydrogen donating property of solvent.

Phenyl ether and dibenzyl were hydrogenated under the same conditions. Compared with benzyl ether, conversions of them were low due to higher bond energy.

It was deduced that decomposition of benzyl ether takes place by the following scheme from the results of this work.



Scheme II

Benzyl ether decomposed to benzaldehyde and toluene accompanied with intramolecular rearrangement of hydrogen without SnO_2 catalyst. Benzaldehyde decomposed consecutively to benzene and reacted with solvent molecule to form HBP compounds such as fluoranthene. On the contrary, the reaction path seems to be different in the presence of SnO_2 catalyst. It was considered that the rate of hydrogenation of intermediate becomes higher than that of rearrangement with SnO_2 . Therefore benzyl ether decomposed to toluene and benzyl alcohol with low selectivity to HBP compounds.

In this paper we discussed the reaction path of hydrogenation of coals and model compounds. It was concluded that tin interacts with fragments of coal and stabilized fragments to prevent recombination reaction.

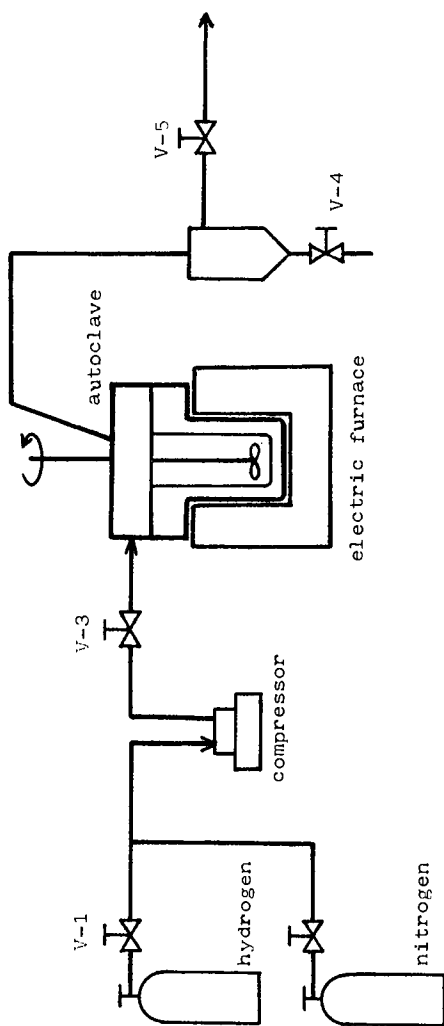


Figure 1. Experimental apparatus

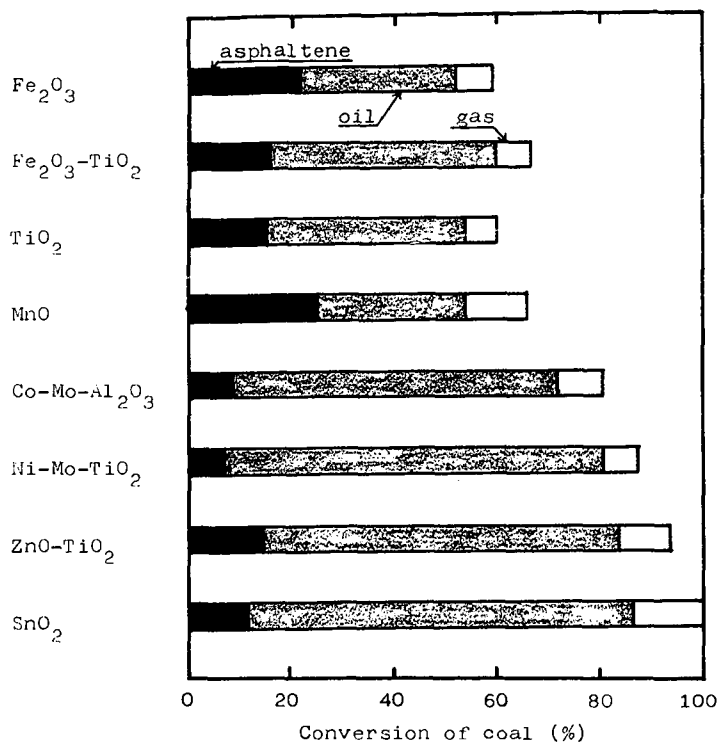


Figure 2. Liquefaction activity of catalysts.
 reaction temperature; 450 C, reaction time;
 30min, H_2 pressure; 150atm

Table 1. Composition of coal.

coal	proximate analysis (%)				ultimate analysis (%)		
	ash	moisture	v.m.	f.c.	C	H	N
Taiheiyō	13.9	5.1	43.8	37.2	63.9	5.6	1.1
Mi-ike	16.2	2.6	37.2	44.0	68.3	5.0	1.1
Da tong	9.7	1.9	23.9	59.5	77.5	4.6	0.9

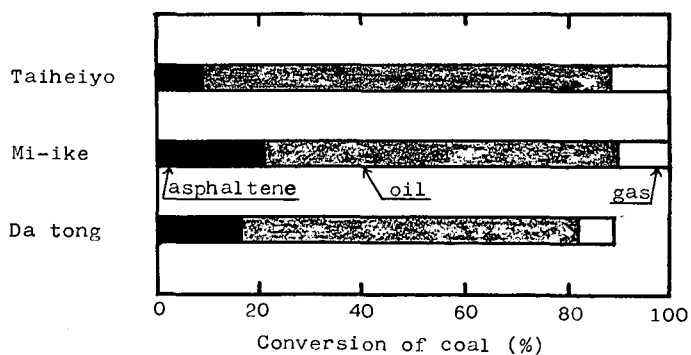


Figure 3. Reactivity of coal with SnO₂.
 reaction temperature; 450°C, reaction time;
 30min, H₂ pressure; 150atm

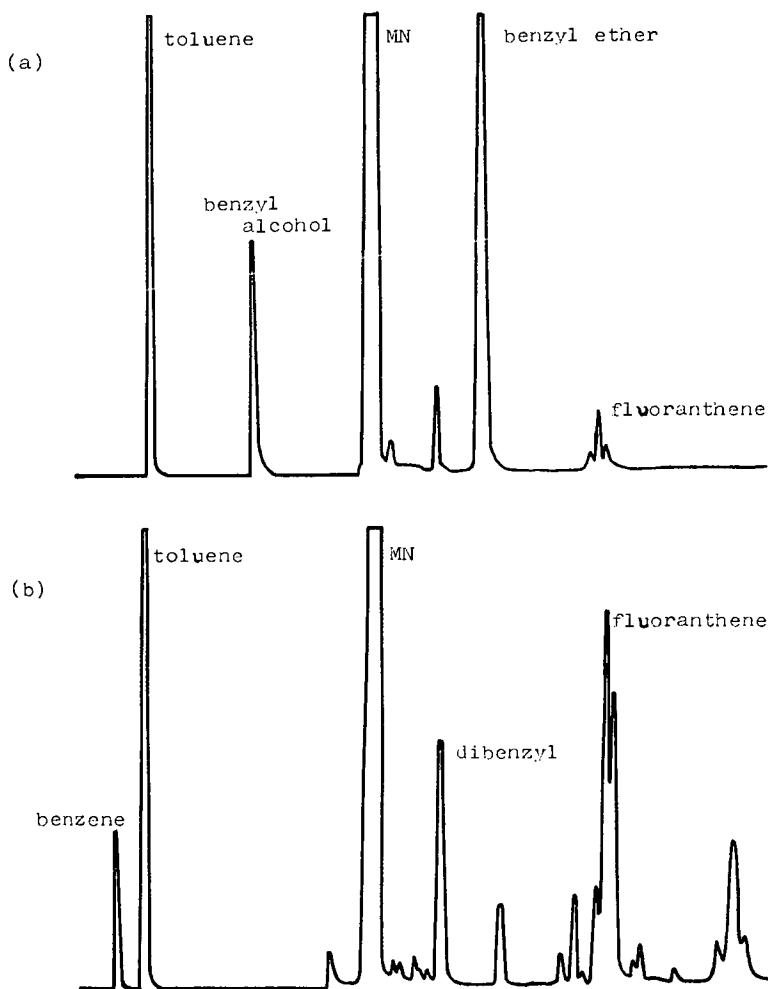


Figure 4. Gaschromatograms of products from hydrogenation of benzyl ether (a) with SnO_2 , (b) without SnO_2 . reaction temperature; 350°C , reaction time; 30min, initial H_2 pressure; 150atm

Table 2. Products from hydrogenation of benzyl ether.

catalyst	solvent	selectivity (%)			
		benzene	toluene	benzyl alcohol	HBP compounds §§
no	MN §	4.7	57.0	0	38.3
	tetralin	2.4	55.8	0	41.8
Ni-Mo-TiO ₂	tetralin	9.9	45.6	0	44.5
SnO ₂	MN	0	51.6	38.4	10.1

§ 1-methylnaphthalene

§§ compounds whose boiling points are higher than benzylether